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(54) Title: LIVING CARBOCATIONIC POLYMERIZATION PROCESS

(57) Abstract

An olefin polymerization process is provided wherein an olefin chargestock is contacted with an organic compound polymerization initiator, a Lewis acid coinitiator and a pyridine compound such as 2,6-di-tert-butylpyridine to produce homopolymers, copolymers or block copolymers having a narrow molecular weight distribution.

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LIVING CARBOCATIONIC POLYMERIZATION PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the polymerization of olefins. The process is a living polymerization process. The term "living polymerization" is used herein to describe a polymerization process which is theoretically terminationless and which is not susceptible to chain transfer.

2. Description of Information Disclosures

Living polymerization processes are known.

U.S. Patent 4,910,321 discloses a living carbocationic polymerization process utilizing initiation systems containing an organic acid or ester and a Lewis acid which may be $TiCl_4$, although the preferred Lewis acid is BCl_3, to produce homopolymers, random copolymers, block copolymers and the like.

U. S. Patent 4,908,421 discloses a living cationic polymerization process for producing a terminally functional polymer utilizing a catalyst system containing a Lewis acid and an organic peroxy compound wherein the monomer charge comprises isobutylene and the organic peroxy compound in an amount ranging from 10^{-4} to 10^{-1} moles per mole of the isobutylene. The Lewis acid may be $TiCl_4$. See also European patent application 8930737377.5 filed July 29, 1989, now Publication No. 0355997 published February 28, 1990.

It has also been proposed to obtain narrow molecular weight distribution polyisobutylenes by utilizing a BCl_3/ester initiator and a 2,6-di-tert-butyl pyridine proton trap.

It has now been found that an olefin polymerization process conducted in the presence of a specified initiator system yields polymers having

improved properties as will become apparent in the ensuing description.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a process for polymerizing an olefin which comprises the step of contacting an olefin chargestock with

(A) an organic compound selected from the group consisting of an alcohol, an ester, an ether, an organic halide and mixtures thereof;

(B) a Lewis acid;

(C) a pyridine compound selected from the group consisting of 2,6-di-tert-butylpyridine, a substituted 2,6-di-tert-butylpyridine, and mixtures thereof,

at polymerization conditions in a polymerization zone, to produce a polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the number average molecular weight ($\overline{M}n$) versus weight in grams of polyisobutylene formed [WPIB(g)] in the polymerization of isobutylene in the presence of a specified initiator system.

Figure 2 is a graph showing the number average molecular weight versus monomer conversion (%) in the polymerization of isobutylene and a specified initiator system.

Figure 3 is a graph showing the number average molecular weight versus monomer conversion (%) in the polymerization of isobutylene using specified initiator systems.

Figure 4 is a graph showing the number average molecular weight versus monomer conversion (%) in the polymerization of isobutylene and a specified initiator system.

Figure 5 is a graph showing number average molecular weight versus weight of polyisobutylene formed (g) in the polymerization of isobutylene and a specified initiator system.

Figure 6 is a graph showing number average molecular weight versus monomer conversion (%) in the polymerization of styrene and specified initiator systems.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention comprises contacting a chargestock containing a single type of olefins or more than one type of olefins in a polymerization zone at polymerization conditions with a initiator system comprising polymerization initiator, herein referred to a Component A, a coinitiator, herein referred to as Component B, and a proton trap, herein referred to as Component C to produce olefin derived polymers having a narrow molecular weight distribution (MWD). The polymerization is a living polymerization process.

The Initiator System

The initiator system comprises Component A, Component B, and Component C.

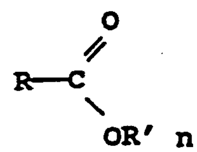
Component A - The Initiator

Component A is an organic compound polymerization initiator selected from the group consisting of an alcohol, an ester, an ether, an organic halide and mixtures thereof. Suitable alcohols include alcohols represented by the formula:

$$R-(OH)_n$$

wherein R is an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, having from 2 to 20, preferably 9 to 15 carbon atoms, and n ranges from 1 to 20, preferably from 1 to 4.

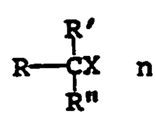
Suitable esters include esters represented by the formula:



wherein R and R′ are independently selected from the group consisting of an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, having from 2 to 20, preferably 9 to 15 carbon atoms, and n ranges from 1 to 20, preferably from 1 to 4.

Suitable ethers include ethers represented by the formula $R\text{-}(\text{-}O\text{-}R')_n$, wherein R and R′ are independently selected from the group consisting of an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, having from 2 to 20 preferably 9 to 15 carbon atoms, an n ranges from 1 to 20, preferably from 1 to 4.

Suitable organic halides include organic halides represented by the formula



wherein R, R′, and R" are each independently selected from the group consisting of an alkyl group, and a substituted alkyl group, an aryl group, a substituted aryl group, having from 2 to 20, preferably 9 to 15 carbon atoms and n ranges from 1 to 20, preferably from 1 to 4, and wherein X is a halogen selected from the group consisting of chlorine, bromine and mixtures thereof. The alkyl group, in the above given formulas may be a saturated alkyl group or an unsaturated alkyl group, e.g. an allyl group.

Component B - The Co-Initiator

Component B is a Lewis acid co-initiator. Suitable Lewis acids include BCl_3, BF_3, $AlCl_3$, $SnCl_4$, $TiCl_4$, SbF_5, $SeCl_3$, $ZnCl_2$, $FeCl_3$, VCl_4 AlR_nCl_{3-n}, wherein R is an alkyl group and n is less than 3, and mixtures thereof. The preferred Lewis acid for use in the present invention is $TiCl_4$. Desirably, the amount of Lewis acid relative to the amount of Component A (initiator) is selected to be at least equal to a stoichiometric amount. Preferably, the number of moles of Lewis acid ranges from about 2 to about 40 times the stoichiometric amount relative to Component A.

Component C

Component C, a proton trap, is a pyridine compound selected from the group consisting of 2,6-di-tert-butylpyridine (DTBP), substituted 2,6-di-tert-butylpyridine and mixtures thereof.

Suitable substituted 2,6-di-tert-butyl-pyridines include 2,6-di-tertiarybutylalkylpyridines such as, for example, 2,6-di-tert-butyl-4-methylpyridine.

When protic impurities (e.g., moisture, acids) are present in the polymerization zone, the pyridine compound is preferably present in at least a stoichiometric amount relative to the protic impurities. More preferably, the pyridine compound is present in an amount greater than the stoichiometric amount relative to the protic impurities.

The Olefinic Chargestock

The olefinic (monomer) chargestock comprises at least a single type of olefin or it may comprise more than one type of olefins depending on the desired final polymer. Suitable olefins include a C_4 to C_7 isomonoolefin, a C_4 to C_{14} multiolefin, a vinylidene aromatic compound which may be substituted or unsubstituted, and mixtures thereof. The preferred C_4

to C_{17} isomonoolefin is isobutylene. The preferred C_4 to C_{14} multiolefin is isoprene.

The preferred vinylidene aromatic compound is selected from the group consisting of styrene, alkylstyrene and mixtures thereof. The preferred alkylstyrenes are a para-methyl-styrene, and an alpha-methylstyrene.

When the olefinic chargestock comprises a C_4 to C_7 isomonoolefin such as isobutylene and a C_4 to C_{14} multiolefin such as a conjugated diolefin, the molar ratio of isomonoolefin to multiolefin may range from about 1000:1 to about 10:1, preferably from about 200:1 to about 40:1.

Block polymers may also be produced by the polymerization of the present invention, for example, by the sequential addition of an isomonoolefin and a second monomer such as a conjugated diolefin (see, for example, U.S. Patent 4,910,261, the teachings of which are hereby incorporated by reference) or a vinylidene aromatic compound.

The process of the present invention may be conducted in the presence or in the absence of a diluent. Suitable diluents include C_1 to C_4 halogenated hydrocarbons, such as methyl chloride and methylene dichloride, C_5 to C_8 aliphatic hydrocarbons, such as pentane, hexane, and heptane and C_5 to C_{10} cyclic hydrocarbons, such as cyclohexane and methyl cyclohexane, and mixtures thereof.

The order of addition of Component A, Component B, and Component C to the olefinic chargestock is not critical. For example, Component A and Component B may be premixed, optionally in a diluent, and added to the olefinic chargestock which may also comprise an optional diluent.

A preferred order of addition is as follows: diluent (if present), olefin chargestock, Component A (initiator), Component C (proton trap), Component B (co-initiator).

The polymerization process is conducted in a polymerization zone of a conventional polymerization apparatus, in the presence or in the absence of a diluent. Suitable polymerization conditions include a temperature ranging from about minus 100°C to about plus 10°C, preferably from about minus 80°C to about 0°C for a time period ranging from about 1 to about 180 minutes (hours). Preferably, the polymerization reaction mixture may be subjected to agitation using conventional mixing means.

The polymers produced by the process of the present invention may be homopolymers, copolymers, terpolymers, etc., block copolymers and the like depending upon the olefinic chargestock used.

The number average molecular weight ($\bar{M}n$) of the polymers of the present invention may range from about 500 to about 2,000,000, preferably from about 20,000 to about 300,000. The polymers have a narrow molecular weight distribution such that the ratio of weight average molecular weight to number average molecular weight ($\bar{M}w/\bar{M}n$) of the polymers ranges from about 1.0 to about 1.5, preferably from about 1.0 to about 1.2. The polymers may be recovered from the polymerization zone effluent and finished by conventional methods.

The following examples are presented to illustrate the invention.

EXAMPLE 1

A series of polymerization experiments were carried out in large test tubes immersed into a heptane bath (-80°C) under nitrogen atmosphere in a MBraun M-150 glove box. Total volume of the reaction mixture was 25 ml. Addition sequence of the reactants was as follows: diluent mixture - monomer - initiator - proton trap - coinitiator. AMI (All Monomer In), and IMA (Incremental Monomer Addition) experiments were carried out. Using the AMI technique, parallel runs

were quenched at different reaction times. From the yield of the polymers and gel permeation chromatography (GPC) data, the percent conversion-time dependencies, $\overline{M}w/\overline{M}n$, and initiator efficiency were obtained. Simultaneously, control runs were carried out in which only the coinitiator and proton trap were charged in the absence of an initiator. Negligible amount of polymer (3%) was obtained in the control runs.

In Example 1, polymerization of IB (isobutylene) was initiated with 5-tert.-butyl-1,3-dicumyl-methylether in the presence of DTBP by the IMA technique. The results are summarized in Figure 1 which shows polymerization of IB initiated with 5-tert.-butyl-1,3-dicumyl-methylether in the presence of DTBP. IMA technique; Time between monomer additions: 30 mins; [t-Bu-DiCuOMe] = 9.25×10^{-4} M; [$TiCl_4$] = 1.48×10^{-2} M; V_o = 25 mL. Diluent: CH_3Cl:n-Hexane, 40:60 v:v; Temperature: -80°C. In Figure 1 number average molecular weight ($\overline{M}n$) is plotted against WPIB (g), that is, weight in grams of polyisobutylene formed and the numbers on the plot are molecular weight distribution (MWD) values.

The IMA method means incremental monomer addition. The AMI method, All Monomer In, means that all the monomer is added before the start of the polymerization, as described in R. Faust, and J. P. Kennedy, J. Polymer Science, Polymer Chem. A25, 1847 (1987).

EXAMPLE 2

Polymerization experiments were also carried out using the AMI technique under the same experimental conditions as in Example 1 utilizing IB chargestock in the presence of DTBP and as initiator 5-tert.-butyl-1,3-dicumyl-methyl ether, as follows: in the presence and in the absence of DTBP, Initiator: 5-tert.-butyl-1, 3-dicumyl-methylether using AMI technique. $[IB]_o$ = 2.04 M [t-Bu-DiCuOMe] = 1×10^{-3} M; [$TiCl_4$] = 1.6×10^{-2} M;

V_o = 25 mL. Diluent: CH_3Cl:n-Hexane, 40:60 (v:v); Temperature: -80°C. The results are summarized in Figure 2 in which number average molecular weight ($\bar{M}n$) is plotted against conversion (%) of the monomer to the polymer.

EXAMPLE 3

In this experiment methylcyclohexane was used instead of n-hexane in the polymerization of isobutylene with the t-BudiCUOMe/$TiCl_4$/CH_3Cl:methylcyclohexane (40:60 v/v), at -80°C system in the absence and presence of a proton trap (DTBP) [t-BudiCUOMe] = 9.24×10^{-4} M; [$TiCl_4$] = 1.48×10^{-2} M. The results are summarized in Figure 3.

EXAMPLE 4

In this example 5-tert.-butyl-1,3-dicumyl-chloride was used as initiator in the polymerization of isobutylene as follows:

Polymerization of IB with 5-tert.-butyl-1,3-dicumyl-chloride as initiator in the presence of proton trap DTBP. AMI technique, $[IB]_o$ = 2.04 M [t-Bu-DiCuCl] = 1×10^{-3} M; [$TiCl_4$] = 1.6×10^{-2} M; V_o = 25 mL. Solvent: CH_3Cl:n-Hexane, 40:60 (v:v); Temperature: -80 °C. The results are summarized in Figure 4.

EXAMPLE 5

In this example IMA technique was followed with 5-tert.-butyl-1,3-dicumyl-chloride as initiator. The experiment was conducted as follows:

Polymerization of IB initiated with 5-tert.-butyl-1,3-dicumyl-chloride. IMA technique (4 x 1 ml); Time elapsed between monomer additions: 30 mins; [t-Bu-DiCuCl] = 1×10^{-3} M; [$TiCl_4$] = 1.6×10^{-2} M; V_o = 25 mL; [DTBP] = 1×10^{-3} M; Diluent: CH_3Cl:n-Hexane, 40:60 (v:v); Temperature: -80°C. The numbers are MWD values. The results are summarized in Example 5.

EXAMPLE 6

In this example styrene was used as monomer as follows:

t-BudiCUOMe/$TiCl_4$/CH_3Cl:MeCH, 40:60 (v:v) system at minus 80°C in the absence and presence of proton trap (DTBP). The results are summarized in Figure 6.

As can be seen from Examples 1 to 6, when the polymerization experiments were carried out in the presence of proton trap (DTBP), deviations from the theoretical line decrease with increasing DTBP concentration and at [DTBP] = 1-2 x 10^{-3} mole/l, close to theoretical molecular weights and narrow MWDs were observed. Independent measurements indicated that this concentration was equal to the concentration of protic impurities in the system.

Preparation of Triblock Copolymers

Based on Examples 1 to 6, related to the living polymerization of isobutylene and styrene, polymerization conditions were obtained under which living polymerization of isobutylene and styrene can be carried out by sequential monomer addition to obtain block copolymers. Block copolymerizations by sequential monomer addition were carried out in a 250 ml three neck flasks equipped with overhead stirrer.

Polymerization parameters:

[Initiator] = 1 x 10^{-3} M

[$TiCl_4$, Coinitiator] = 1.6 x 10^{-2} M

[DTBP] = 2 x 10^{-3} M

Diluent: MeCl/methylcyclohexane (40/60 v/v)

Temperature: -80°C

Isobutylene added: 12 ml (= 8.4 g)

Styrene added: 3.9 ml

Styrene polymerization time: 5 minutes

The method of monomer addition strongly affects the outcome of styrene polymerization: Using pure (undiluted) styrene leads to temporary freezing of this monomer at the moment of addition into the -80°C solution. Freezing can be eliminated by diluting the monomer. Using methylcyclohexane in volume ratio 1:4 (3.5 ml styrene + 14 ml MeCH) the polar/apolar volume ratio of the reaction medium changed from 40:60 in favor of the apolar components (MeCH and St) at the beginning of St (styrene) polymerization. The properties of triblocks obtained can be compared from the stress-strain data.

EXAMPLE 7

In this example, 5-t-butyl-1,3-bis(1-methoxy-1-methylethyl) benzene initiator was used; undiluted styrene was added, and the DTBP concentration was 1 x 10^{-3} M.

Sample No.	PSt	PIB	PSt	$\overline{M}w/\overline{M}n$
A	15500	85000	15500	1.43

PSt means polystyrene

PIB means polyisobutylene

$\overline{M}w/\overline{M}n$ is the ratio of weight average molecular weight to number average molecular weight.

EXAMPLE 8

In this example, 5-t-butyl-1,3 bis (1-acetoxy-1-methylethyl) benzene initiator was used; styrene was added undiluted.

Sample No.	PSt	PIB	PSt	$\overline{M}w/\overline{M}n$
B	14300	78000	14300	1.53

EXAMPLE 9

In this example, 5-t-butyl-1,3 bis (1-chloro-1-methylethyl) benzene initiator was used; styrene was diluted with methyl cyclohexane (1/4; v/v) and the DTBP concentration was 1×10^{-3} M.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
C	8066	70900	8066	1.13

EXAMPLE 10

In this example, same initiator was used as initiator used in Example 9; styrene was diluted with methyl cyclohexane (1/4; v/v).

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
D	7082	82500	7082	1.11

EXAMPLE 11

In this example, same initiator as in Example 9 was used; styrene was diluted with methyl cyclohexane (1/4; v/v) and the DTBP concentration was 4×10^{-3} M.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
E	7154	78200	7154	1.21

EXAMPLE 12

In this example, same initiator as in Example 9 was used; styrene was diluted with methyl cyclohexane (1/4; v/v), and the styrene reaction time was 10 minutes.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
F	14400	84000	14400	1.19

EXAMPLE 13

In this example, same initiator as in Example 9 was used; styrene was diluted with methyl cyclohexane

(1/4; v/v), the polymerization temperature was minus 90°C, and the styrene reaction time was 10 minutes.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
G	6380	80300	6380	1.19

EXAMPLE 14

In this example, same initiator as in Example 9 was used; styrene was diluted with methyl cyclohexane (1/4; v/v), and the styrene reaction time was 15 minutes.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
H	13900	89300	13900	1.13

EXAMPLE 15

In this example, same initiator as in Example 9 was used; styrene was diluted with methyl cyclohexane (1/4; v/v), the polymerization temperature was minus 90°C, and the styrene reaction time was 15 minutes.

Sample No.	PSt	PIB	PSt	$\bar{M}w/\bar{M}n$
I	14600	86900	14600	1.12

The Stress-Strain data are summarized in Table I.

TABLE I

Stress-Strain Data

Sample No.	100% Mod.	300% Mod.	500% Mod.	Tensile Strength psi	Elongation %
A	110	347	1084	1830	625
B	112	322	931	2195	615
C	45	55	84	490	1000
D	63	114	237	1898	865
E	40	75	135	725	850
F	85	221	947	2700	650
G	44	35	52	75	850
H	88	200	890	3000	690
I	85	197	967	3600	750

The test methods used are shown in Table II.

TABLE II

Property	Test Method
100% Modulus, psi	ASTM D412
300% Modulus, psi	ASTM D412
500% Modulus, psi	ASTM D412
Tensile Strength, psi	ASTM D412
Elongation, %	ASTM D412

EXAMPLE 16

In this example, 1-chloro, 2,4,4-trimethyl pentane was used as initiator. [M] = 2.0 M, [I] = 5.1×10^{-2} M, [$TiCl_4$] = 1.2×10^{-1} M, [DTBP] = 2×10^{-3} M, temperature = -40°C, solvent: n-hexane-CH_3Cl 60/40 v/v. The PIB prepared this way had M_n = 2200, MWD = 1.14.

EXAMPLE 17

In this example, 2-chloro, 2-phenyl propane was used as initiator. [M] = 3.7 M, [I] = 9.44×10^{-2} M, [$TiCl_4$] = 1.9×10^{-1} = [DTBP] = 2×10^{-3} M, temperature = -60°C, solvent: n-hexane-CH_3Cl, 60/40 v/v.

a) The PIB obtained by the AMI technique exhibited M_n = 2300, MWD = 1.3.

b) The PIB prepared by continuously feeding isobutylene, equivalent to the amount in example 16, to the solution containing the initiator, coinitiator and DTBP exhibited MWD = 1.08.

CLAIMS:

1. A process for polymerizing an olefin which comprises the step of contacting an olefin chargestock with

(A) an organic compound selected from the group consisting of an alcohol, an ester, an ether, an organic halide and mixtures thereof;

(B) a Lewis acid comprising $TiCl_4$; and

(C) a pyridine compound selected from the group consisting of 2,6-di-tert-butylpyridine, a substituted 2,6-di-tert-butylpyridine, and mixtures thereof;

at polymerization conditions in a polymerization zone, to produce a polymer.

2. The process of claim 1, wherein protic impurities are present in said polymerization zone and wherein said pyridine compound present in said zone is at least a stoichiometric amount relative to said protic impurities.

3. The process of claim 2, wherein said said pyridine compound present in said zone is greater than the said stoichiometric amount relative to said protic impurities.

4. The process of claim 1, wherein said substituted 2,6-di-tert-butyl pyridine is 2,6-di-tert-butyl-4-methyl-pyridine.

5. The process of claim 1 wherein said Lewis acid is $TiCl_4$.

6. The process of claim 5, wherein the number of moles of said $TiCl_4$ in said polymerization zone is present in at least a stoichiometric amount relative to said (A) organic compound.

7. The process of claim 5, wherein said number of moles of said $TiCl_4$ ranges from about 2 to 40 times stoichiometric amount relative to said (A) organic compound.

8. The process of claim 1, wherein said olefin chargestock comprises an olefin selected from the group consisting of C_4 to C_7 isomonoolefin, C_4 to C_{14} multiolefins a vinylidene aromatic compound and mixtures thereof.

9. The process of claim 8, wherein said vinylidene aromatic compound is styrene.

10. The process of claim 8, wherein said vinylidene aromatic compound is an alkylstyrene selected from the group consisting of alpha-methylstyrene, para-methylstyrene and mixtures thereof.

11. The process of claim 1, wherein said organic compound is an organic halide.

12. The process of claim 1, wherein said polymerization conditions include a temperature ranging from about minus 100°C to about plus 10°C.

13. The process of claim 1, wherein said polymerization zone additionally comprises a diluent.

14. The process of claim 13, wherein said diluent is selected from the group consisting of C_1 to C_4 halogenated hydrocarbons, C_5 to C_8 aliphatic

hydrocarbons, C_5 to C_{10} cyclic hydrocarbons, and mixtures thereof.

15. The process of claim 1, wherein said polymer has a number average molecular weight ranging from about 500 to about 2,000,000.

16. The process of claim 1, wherein said polymer has a number average molecular weight ranging from about 20,000 to about 300,000.

17. The process of claim 1, wherein said polymer has a narrow molecular weight distribution.

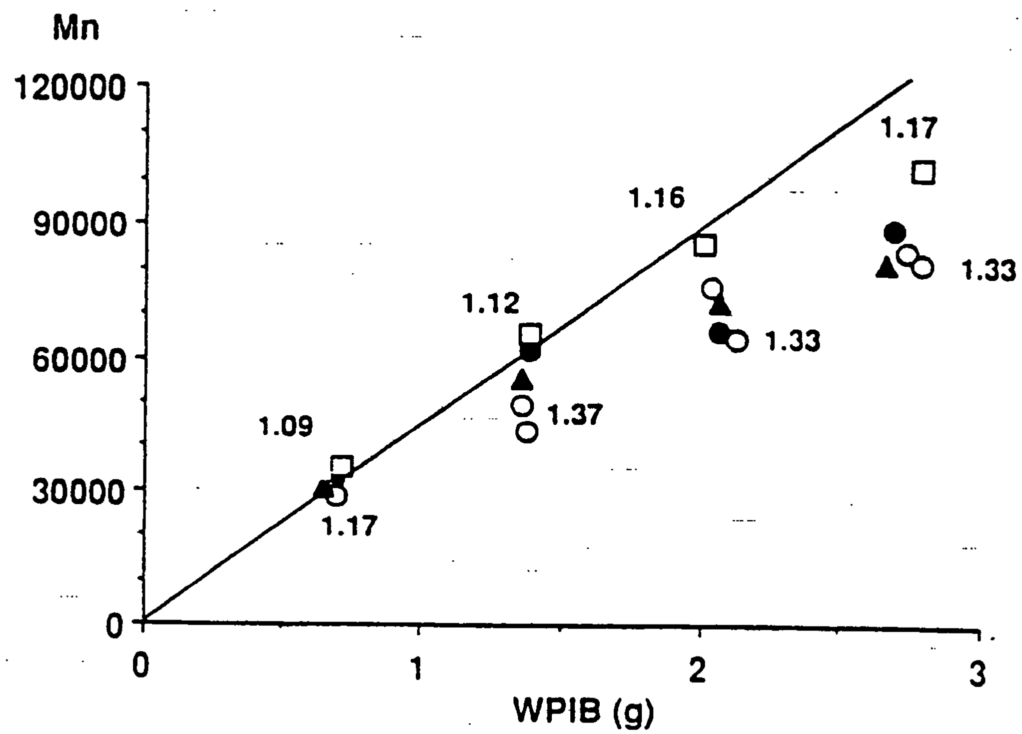

Mn
120000
90000
60000
30000
0
0
1
2
3
WPIB (g)
1.09
1.17
1.12
1.37
1.16
1.33
1.17
1.33

FIG. I

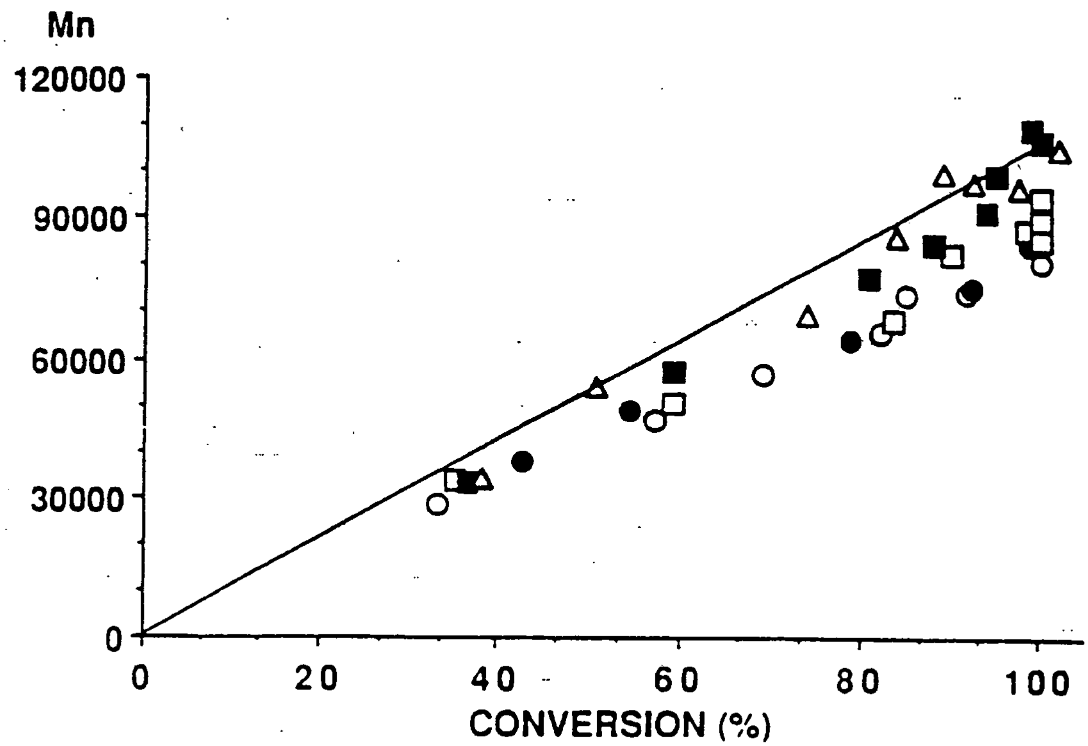
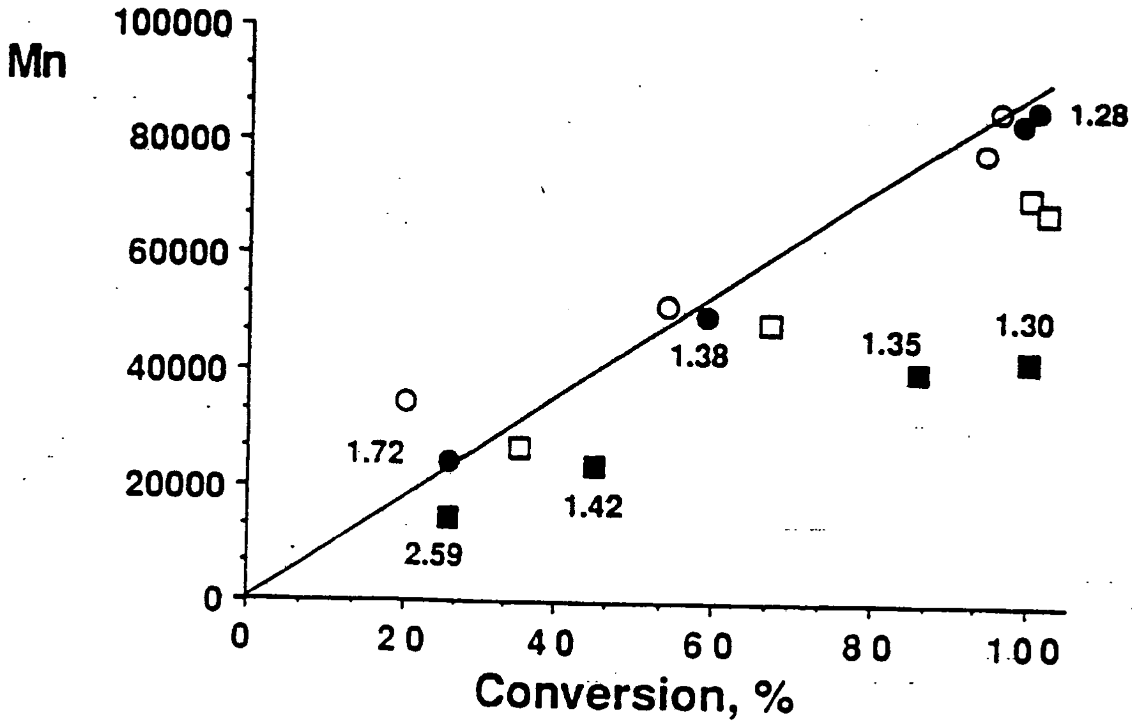


FIG. 2


Mn
100000
80000
60000
40000
20000
0
0
20
40
60
80
100
Conversion, %
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1.72
1.42
2.59

FIG. 3

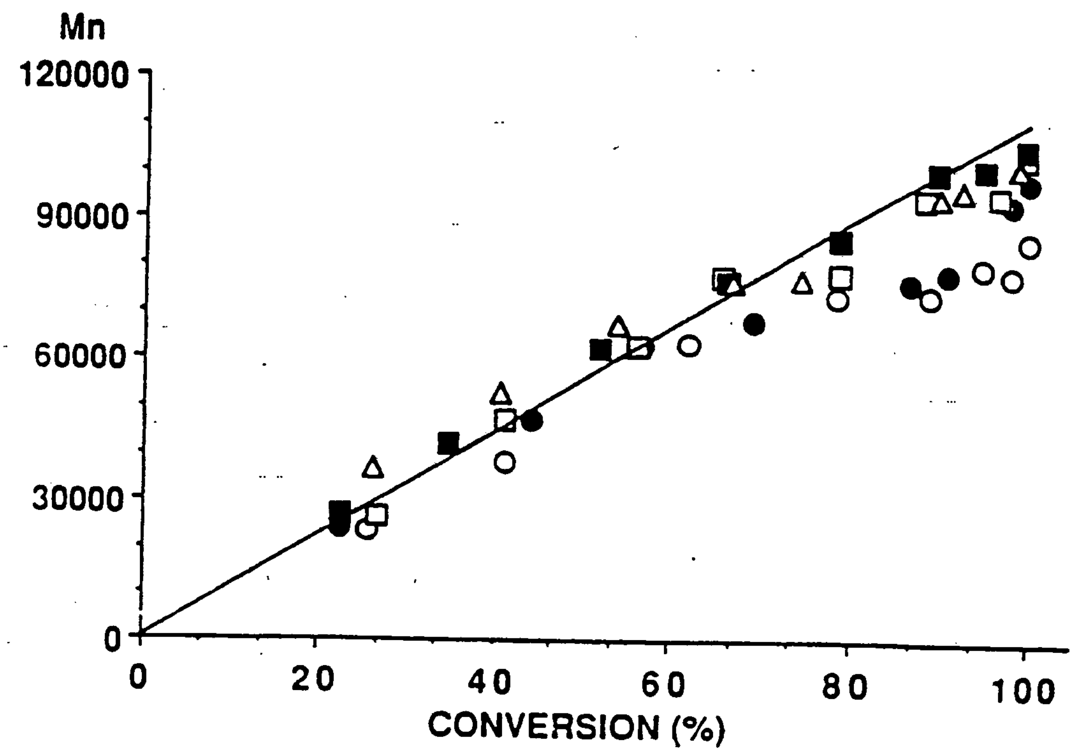
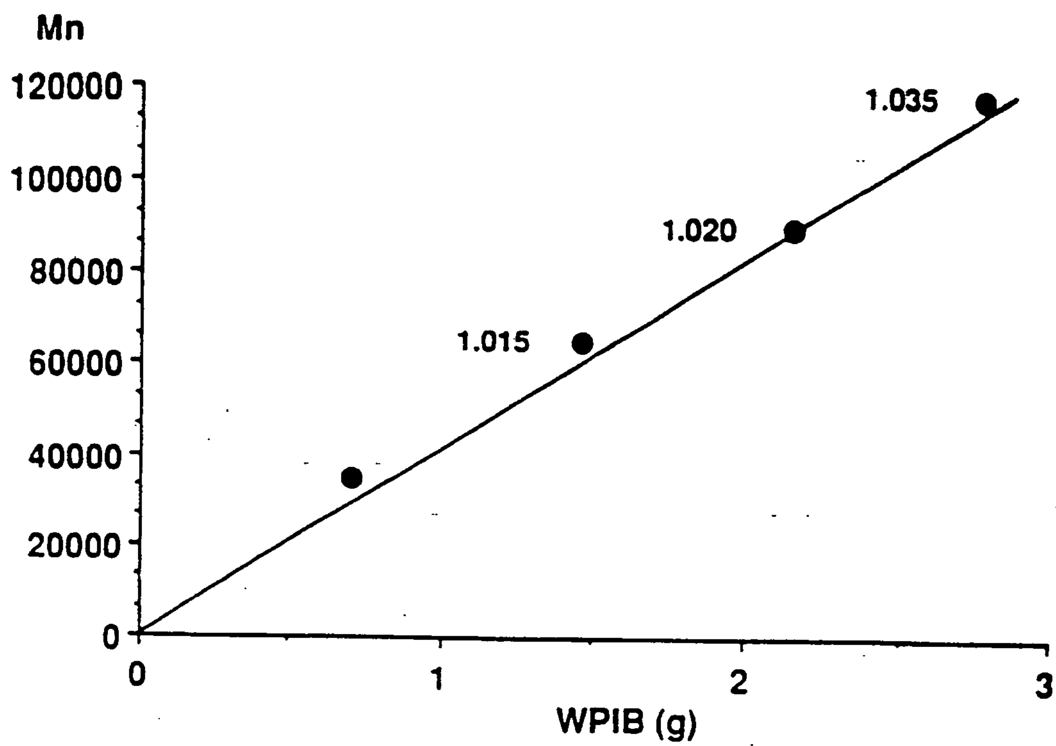
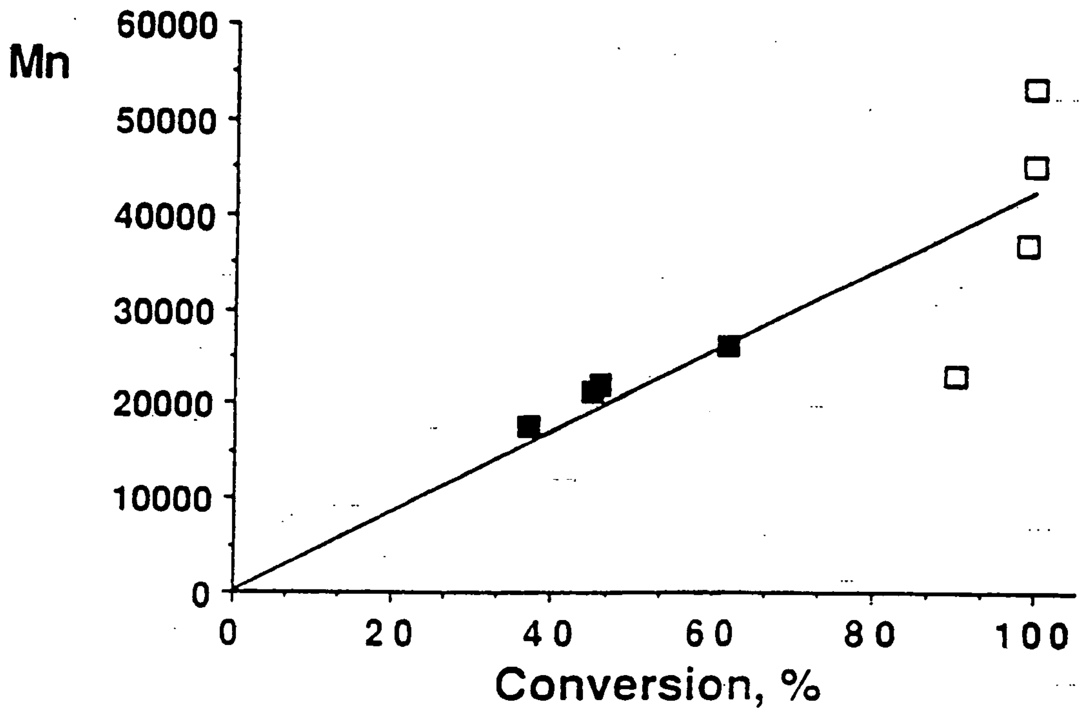


FIG. 4



Mn
120000
100000
80000
60000
40000
20000
0
0
1
2
3
WPIB (g)
1.035
1.020
1.015

FIG. 5


Mn
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50000
40000
30000
20000
10000
0
0
20
40
60
80
100
Conversion, %

FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/05366

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 08 F 4/649, C 08 F 10/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC^5	C 08 F 4/00, C 08 F 10/00, C 08 F 12/00, C 08 F 297/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[*]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4 946 899 (KENNEDY et al.) 07 August 1990 (07.08.90), see claims 1-3,5-12; examples.	1-17
X	Journal of Macromolecular Science-Chemistry, vol. A18, no. 1, issued 1982 (Dekker Journals, New York), J.P. KENNEDY et al. "Carbocationic Polymerization in the Presence of Sterically Hindered Bases", see pages 1-152.	1-17
A	EP, A2, 0 397 081 (NIPPON ZEON CO., LTD.) 14 November 1990 (14.11.90), see claims 1,4,5; examples.	1-3,5-17

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
01 October 1992	19. 10. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PUSTERER e.h.

ANHANG	ANNEX	ANNEXE
zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.	to the International Search Report to the International Patent Application No.	au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 92/05366 SAE 61847

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.	This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.	La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4946899	07-08-90	keine - none - rien	
EP A2 397081	14-11-90	JP A2 3174403	29-07-91
		EP A3 397081	12-02-92